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**(54) Improving Interfacial Bond of  
Moulded Composite Articles**

(57) A process for the manufacture of a plastics article which comprises bringing at least two plastics into contact with one another and shaping them and bonding them to one another at the contact surface, wherein at least one of the two plastics comprises components which react with one another during the shaping, at least in the region of the contact surface, and the other of the two plastics in the liquid state during

the shaping, at least in the region of the contact surface, and wherein at least one of the reactive components has a pronounced tendency to diffuse into the other plastic. The diffusing component may be a monomer or low-molecular weight constituent of one plastic and a solvent for the other plastic. The composite article may be formed by injection or extrusion moulding. One plastic may be a thermosetting polyester and the other plastic may be polystyrene or polymethyl methacrylate. The polyester may be reinforced with glass fibres.

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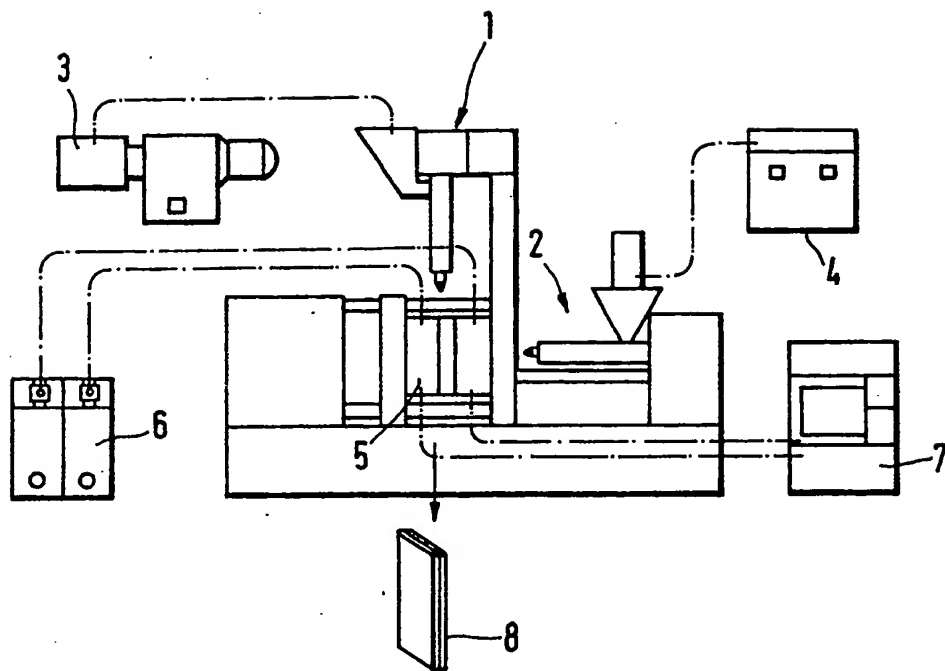
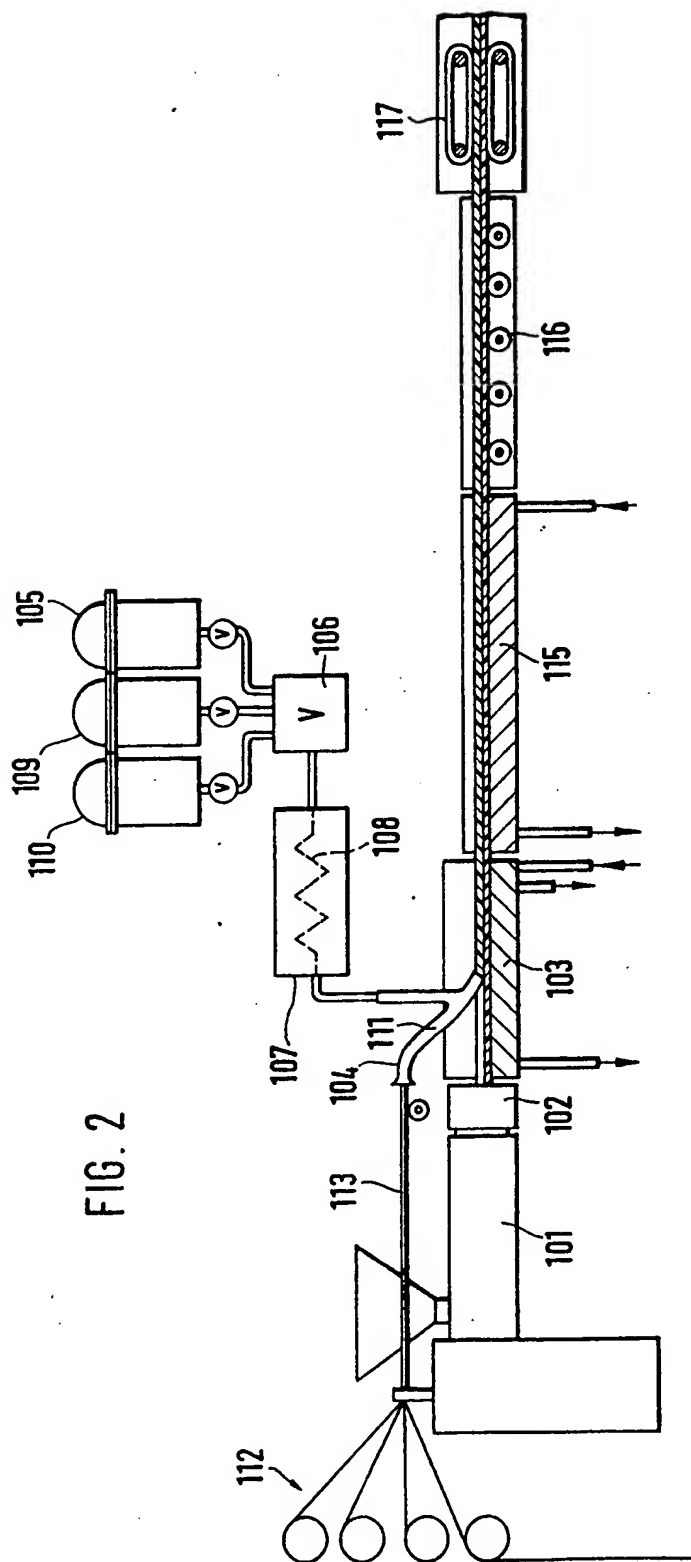


FIG. 1

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## SPECIFICATION

## Process for Manufacturing Bonded Plastics Articles

The invention relates to a process, especially  
 5 an injection moulding process or extrusion process, for the manufacture of plastic articles having a bonded construction in which at least two plastics having different properties are, during moulding of a plastics article, brought into  
 10 contact with one another and bonded to one another at a contact surface, with at least one of the two plastics consisting of components which react with one another during moulding, at least in the region of the contact surface, whilst the  
 15 other plastic is in the liquid state, especially the molten state, in the region of the contact surface.

A process of the type outlined above is described in our earlier Patent Application No. 15164/77 and includes the feature that the  
 20 joining process, that is to say the process in which different plastics are bonded to one another at one or more contact surfaces, takes place while at least one plastic is in the reactive stage whilst the other, unless it is also undergoing curing, is in the form of a plastic melt. In this context, reaction or  
 25 reactive stage is to be understood as any state in which identical or different components undergo chemical bonding to one another, thus including, in particular, any type of polymerisation. This  
 30 achieves a particularly intimate bond between the two plastics of the bonded article, and, according to an advantageous embodiment of the process according to the earlier proposal, the polymerisation progresses to different extents  
 35 over the thickness of one of the plastics layers. The bonding phenomena which occur at the contact surface have hitherto not been unambiguously elucidated, but it is to be assumed that both a mechanical interlacing and chemical  
 40 reactions between the bond partners occur and that possibly other physical phenomena (e.g. adhesion) participate.

The present invention is now directed towards an improvement of the process according to the  
 45 earlier proposal, which contributes to achieving a more intense bond in the region of the contact surface.

The invention accordingly provides a process for the manufacture of a plastics article which comprises bringing at least two plastics  
 50 into contact with one another and shaping them and bonding them to one another at the contact surface, wherein at least one of the two plastics comprise components which react with one another during the shaping, at least in the region of the contact surface, and the other of the two plastics is in the liquid state during the shaping, at least in the region of the contact surface, and wherein at least one of the said reactive  
 55 components has a pronounced tendency to diffuse into the other plastic.

As a result of the tendency of at least one component of the reactive plastic to diffuse into the other plastic, the mechanical interlacing

65 between the plastics is intensified and hence leads to greater bond strengths. Advantageous combinations are, for example, those wherein one of the reacting components is a low-molecular weight constituent or a monomer of one plastic  
 70 and at the same time a solvent for the other plastic. This applies, for example, when processing unsaturated polyesters as the reactive plastic and polystyrene as the other.

In a further embodiment, it can even prove  
 75 advantageous to employ an excess of the particular component of the reactive plastic which has the pronounced tendency to diffuse. This can have the consequence that copolymerisation reactions and/or grafting reactions occur in the  
 80 region of the contact surface, so that the bond strength can be controlled by deliberate variation of such reactions.

If, for example, the material combination of unsaturated polyester casting resin and  
 85 polystyrene is selected for a bonded article, it can be assumed that in the state in which these materials encounter one another when carrying out the process according to the invention, the heat-curing unsaturated polyester resin is in the  
 90 gel state and consists of the following components: polyester, monomeric styrene, short-chain homopolymerised polystyrene (radical chain polystyrene), copolymerised styrene and possibly also free peroxide radicals. The  
 95 polystyrene, constituting the second plastic, is present as a melt at about 200°C. The molecular lattice is loosened since intermolecular forces have only a relatively weak effect at this temperature. It is also to be expected that part of  
 100 the thermoplastic chains are present as chain fragments which are formed, as a result of heat exposure, during any melting and plasticising process.

If now the polystyrene melt encounters the  
 105 above-mentioned heterogeneous mixture of the reactive phase, the low-molecular weight constituents of this mixture can diffuse, in the gel state, into the polystyrene melt. The diffusion process is substantially favoured by the high  
 110 mobility of the polystyrene chains in the melt. Monomeric styrene, which is a good solvent for polystyrene even at room temperature, can at the same time penetrate into deeper layers of the reactive phase. This possibility also exists for the  
 115 short chain radicals and for homopolymer chains. In the further course of the crosslinking of the reactive phase, the constituents which have penetrated participate in the reaction of the said phase and lead, in the boundary layer, up to a  
 120 certain depth below the contact surface, to an interlacing in which chains of the two partners of the bond are entangled.

The above-mentioned simultaneously occurring copolymerisation reactions and graft  
 125 polymerisation reactions between the chain segments of the polystyrene and the resin constituents present in the gel state have the effect of increasing the strength of the bond.

Examples of embodiments are given below in order to illustrate the invention:

#### Example 1

To produce a bonded article in the shape of a flat sheet of size 110×190×6 mm by the injection moulding process, a three-plate mould with a slide which can be moved into, and out of, the mould cavity was used. The participant plastics used for the bonded article were a thermosetting resin, in the form of an unsaturated polyester resin, and polymethyl methacrylate (PMMA). The thickness of the layer of thermosetting resin should be 4 mm and that of the thermoplastic layer 2 mm.

The unsaturated polyester resin was injected at room temperature into the part of the mould cavity on the clamping side, in which part the mould was kept at a temperature of 150°C. At this point in time, the slide has been introduced into the mould cavity. Following an injection time and holding-pressure time for 110 seconds, a reaction time of 35 seconds was allowed before venting the mould and withdrawing in the slide. This was followed by injecting the PMMA into the part of the mould cavity on the nozzle side, which part was kept at a temperature of 90°C. On entering the mould cavity, the PMMA was at a temperature of about 200°C. After a cooling time of 30 seconds, it was possible to open the mould and to inject the finished bonded article.

The pressures maintained on injecting the polyester resin and the PMMA were 10 bars and about 800 bars respectively.

A bonded article of great strength was obtained, in which the participant plastics were inseparably bonded to one another.

Instead of using pure unsaturated polyester resin, it is readily possible to employ a filled polyester resin. For example, using the same process steps as mentioned above, it is possible to use a reactive phase having the following composition: 100 parts of low profile unsaturated polyester resin (Leguval 7125 from Bayer AG), 100 parts of quartz powder as a filler, 2 parts of peroxide (Trigonox 29B 50 from Akzo-Chemie) and 1 part of coloured pigment.

To carry out the process example described above, the injection moulding machine shown schematically in Figure 1 was used. This comprises two injection units 1 and 2 for the unsaturated polyester resin and the PMMA respectively, arranged with their injection cylinders at right angles to one another. To compound the unsaturated polyester resin, a mixer 3 is provided, which feeds injection unit 1; the PMMA granules are located in a granule dryer 4, from which the granules are conveyed to the injection unit 2. The three-plate mould 5 is shown schematically. The injection moulding machine includes temperature-control instruments 6, the connection of which, for the purpose of maintaining the temperatures of the mould halves mentioned in the Example, is shown in dot-dash lines. A measuring stand 7, for monitoring and

recording the process parameters, is provided, and its connection to the parts of the injection moulding machine 1 is also drawn in dot-dash lines.

As a result of the injection units 1, 2 being arranged at right angles to one another, the PMMA is applied at right angles onto the contact surface of the polyester resin layer. Because of the temperature spread of the mould (temperature gradient 60°C), a directional reaction took place in the polyester resin layer, so that the reaction was virtually complete on the wall side during the process of injecting the PMMA, whilst in the region of the contact surface the polyester resin was still in the gel state.

The resulting bonded article 8 is shown schematically.

#### Example 2

An elongate ribbon-shaped bonded article 42 mm wide and 8 mm thick was produced by an extrusion process. The bonded article possessed a trough-shaped base layer of polystyrene (482 G from BASF AG), made up to a rectangular cross-section by means of a layer, filled into the trough, of unsaturated polyester resin of the same type and composition as in Example 1. The polystyrene was extruded at an extrusion temperature of 170°C; the extrusion rate was 3 meters/minute. The unsaturated polyester resin mixture was supplied by means of a casting device and was applied to the polystyrene base layer immediately behind the nozzle orifice. In this illustrative embodiment, the polyester resin mixture was pre-warmed to a temperature of 90° to 100°C. After bonding of the two plastics, the extruded ribbon was calibrated in a vacuum device, fully cured and cooled.

Figure 2 schematically shows an extrusion installation in which process Example 2, described above, was carried out:

Downstream from a screw extruder 101, having an extruder die 102 for the polystyrene base layer, is located a vacuum and cooling device 103 combined with a feed device 104 for the polyester resin. The polyester resin is supplied to the feed device 104 from a container 105 via a valve 106 and a coil 108 located in a heating bath 107. Further containers 109 and 110 contain a cleaning agent and flushing resin, which can be delivered, for the purpose of cleaning the coil 108 and the feed device 104, by appropriately setting the valve 106.

The feed device 104 possesses a pipe branch 111, through which glass fibre rovings 113 are supplied from an unwind device 112. The glass fibre rovings are impregnated with the polyester resin, supplied through the coil 108, whilst they are still within the feed device 104, and are laid down, together with the polyester resin, on the extruded polystyrene base layer. It is advantageous to pre-warm the glass fibre rovings 113 to match them to the temperature of the polyester resin.

The vacuum and cooling device 103 is

followed by a cooling and reaction zone 115, in which the extrudate is cooled and the polyester resin laminated onto it is cured. Further curing takes place in a subsequent reaction zone 116 in the form of a roller track from which the finished product is then drawn off by means of a caterpillar take-off 117.

Using the process according to the invention, it is even possible to combine relatively brittle plastics with ductile plastics. It has been found that bonding such plastics results in an apparent change in the material characteristics, with the brittle characteristics of one bonding partner being ameliorated, without loss in strength.

The different heat expansion characteristics of the participant materials can be taken into account by suitable selection of the formulation, for example of the monomer system of the reactive plastic, since it is thereby possible to influence the shrinkage characteristics during reaction and match them to the thermal shrinkage characteristics of the other plastic. Possible ways of selecting this formulation are an appropriate choice of the nature and amount of catalysts and/or activators. It is also possible to match the nature and amount of the reactive plastic used to the other plastic. Finally, it is possible to influence the heat expansion characteristics of both the reactive plastic and the other plastic by using suitable fillers and reinforcing agents in a defined amount.

It is also possible to conduct the reaction of the reactive plastic, by suitable temperature control, in such a way as to permit matching to the expansion characteristics of the other bonding partner. For example, it is conceivable to influence the temperature in the interior of the layer which is in the reactive state, by high frequency heating. Such heating also suggests itself if a contact surface in the gel state is to be created on both sides of the layer which is in the reactive state, since with this type of introduction of thermal energy, the higher temperatures occur in the interior of the layer.

The particular matching of the shrinkage characteristics of the bonding partners during the joining process is effected on the basis of the known heat expansion coefficients or shrinkage coefficients and on the basis of a knowledge of the shrinkage which occurs during the reaction of the reactive phase.

The pressure and temperature of the participant bonding partners can be set in accordance with experience gathered in processing these partners individually. As far as the pressure is concerned, the general rule is that the pressure is set, in respect of the reactive

plastic, so that it exceeds the vapour pressure of the low-molecular weight or monomeric constituents at the particular temperature, in order to prevent these constituents from evaporating. In addition, an elevated pressure may be used in order to allow intermolecular forces to become effective in the region of the contact surface.

Various parameters can be employed to optimise the process according to the invention; the reaction and the interfacial activity, can be most effectively influenced by these parameters. The most suitable parameter to select is the temperature difference by means of which the "gradient" of the reaction in the reactive plastic can be adjusted, as well as the reaction time before joining the partners, that is to say before applying the other plastic, and, finally, also the excess of the particular reactive component which possesses a pronounced tendency to diffuse into the other plastic.

#### Claims

1. A process for the manufacture of a plastics article which comprises bringing at least two plastics into contact with one another and shaping them and bonding them to one another at the contact surface, wherein at least one of the two plastics comprises components which react with one another during the shaping, at least in the region of the contact surface, and the other of the two plastics is in the liquid state during the shaping, at least in the region of the contact surface, and wherein at least one of the said reactive components has a pronounced tendency to diffuse into the other plastic.

2. A process according to claim 1, wherein one of the said reactive components is a low-molecular weight constituent or a monomer of one of the two plastics, and is at the same time a solvent for the other plastics.

3. A process according to claim 1 or 2, wherein the reactive component having the said pronounced tendency to diffuse is present in excess.

4. A process according to claim 1 substantially as described in the foregoing Example 1 or 2.

5. An injection moulding machine for carrying out the process according to any one of claims 1 to 4, with at least two injection units, wherein the mould has at least one removable slide which subdivides the mould cavity into two part-cavities and in that the injection units are each in communication with one of the part-cavities.

6. A machine according to claim 5 substantially as described with reference to Figure 1 of the accompanying drawings.

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⑪ 特許出願公開

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(全 4 頁)

⑮ 射出吹込成形における2層パリソン成形法

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⑱ 特 願 昭53—110363

⑲ 出 願 昭53(1978)9月8日

⑳ 発 明 者 中村喜則

明 細 書

1. 発明の名称

射出吹込成形における2層パリソン成形法

2. 特許請求の範囲

(1) パリソンを2層に射出成形してのち、所望の中空成形品に吹込成形するにあたり、キャビティと冷却手段を内蔵したコアとの間に熔融樹脂を射出して外層パリソンを成形し、次に上記コアと先端に射出口を有し内部に熔融樹脂通路を備えた射出コアとを交換し、該射出コアと外層パリソンとの間に射出を行つて内層パリソンを成形することを特徴とする射出吹込成形における2層パリソン成形法。

(2) 外層パリソンの射出成形に際し、外層パリソンのゲート部分を、冷却手段を内蔵したコアにより他の部分よりも冷却する特許請求の範囲第1項記載の射出吹込成形における2層パリソン成形法。

3. 発明の詳細な説明

この発明は2層からなる中空成形品を射出吹込成形する場合に必要な2層パリソンの成形法に関するものである。

従来の2層パリソンの成形は、特公昭46-29980号公報に開示されているように、予め成形した合成樹脂成形体を吹込みコアに被せ、その外側に外層パリソンを射出成形するか、または実公昭47-16620号公報に開示されたように、内層パリソンの射出成形を先行し、この内層パリソンをコアと共に他のキャビティに移送して、外層パリソンを射出成形するかして行つていた。

上記インサートによる2層パリソンの成形法にあつては、パリソンの成形に際して内層となる成形体をコアに一々被せねばならず、また完全に固化した成形体に、熔融樹脂による外層パリソンを射出した場合の両者の温度分布は一様ではなく、全体的に吹込成形に適した温度分布を得るには、他に技術や経験が必要とされている。

またすべてを射出成形による方法では、上記イ

ンサートのごとき問題はないが、内層パリソンと外層パリソンを成形する2個のキャビティが必要となる。しかも完全固化していない内層パリソンに向けて射出を行うため、内層パリソンのゲートに臨む部分が溶解して混り合い、時には他の部分にも融合が生ずることから、内層パリソンの肉厚を薄くすることができないなどの欠点があった。

この発明は、外層パリソンの射出成形を先行し、コアの交換により外層パリソンの成形に用いたキャビティを、そのまま内層パリソンの成形に利用して、上記従来法よりも精度が高く、また成形した2層パリソンの温度を、吹込みに適した温度に維持することができる新たな成形法を提供するのである。

以下この発明を図示の例により詳細に説明する。

図中1はヒータまたは加熱オイル路2を埋設したパリソン射出成形用のキャビティ、3は外層パリソン成形用のコアで、冷却手段が内蔵してある。この冷却手段は中空のコア3の中央に挿入した水管4と、コア3の中空部とによつて形成された冷

却水路5からなり、かつ水管4の開口端はベースプレート6の水路からの冷却水をキャビティ1のゲート1aに臨むコア先端部に向け噴きつけて、他の部分よりも冷却すべくコア先端の内面に対向させて設けてある。

7は内層パリソン成形用のコアで、上記コア3よりも細い中空体の先端に射出口8を有し、かつ基部周囲に開閉自在なエア通路9を具備する。また内部にはトービード10の挿入により形成した溶融樹脂の通路11があり、その通路11はベースプレート12のノズルタッチ部と接続している。

次に2層パリソンの成形工程を順に説明する。

第1図、所定温度に加熱したキャビティ1とコア3とを型締し、ゲート1aのノズル13からキャビティ内に溶融樹脂を射出して、外層パリソン14aを成形する。この外層パリソン14aの内側は、内部に冷却水を流通させたコア3により冷却を受け、キャビティ1と接する外側よりも温度が低くなつてスキン層を形成する。特に外層パリソン14aのゲート部分は、他の部分よりも冷却されるこ

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とから、射出完了後にノズル13を離したのちには、冷却が外側にまで及んで一部分的に固化する。

第2図、上記スキン層によつて外層パリソン14aから、コア3を離型できるようになつたら、キャビティ1はそのままにしてコア3を抜き外し、外層パリソン14aをキャビティ1に残す。

第3図、次にコア3を射出コア7と交換し、型面に外層パリソン14aが張り付いた上記キャビティ1に、射出コア7を挿入して型締を行う。この射出コア7は先にも述べたように、コア3よりも細く形成してあることから、射出コア7の周囲には、外層パリソン14aの底部よりベースプレート12にて閉塞されたキャビティ1のネック型部分1bに至る成形空間15が形成される。

第4図、上記射出コア7のベースプレート12に設けたゲート12aにノズル16をタッチして、射出コア7の先端より成形空間15に、溶融樹脂を射出し、外層パリソン14aの内側にネック部14cを同時成形した内層パリソン14bを成形する。

この場合、射出コア7の射出口8が、外層パリ

ソン14aの内底部に対向していても、外層パリソン14aの底部は固化状態にあるので、射出圧と溶融樹脂の熱を受けて軟化しても、著しく溶解するようなことがなく、他の部分もスキン層によつて形状を保つ。このため、そこに形成された2層パリソン14は、内外層が互に接着してはいても融合せず、それぞれ独立した状態にある。

第5図及び第6図、キャビティ1を開き、内層パリソン14bによつて全体が加熱軟化した2層パリソン14を、射出コア7と共に吹込キャビティ17に移送し、型締後に、射出コア7のエア通路9を開いて射出コア7と内層パリソン14aとの間にエアを吹込み、吹込キャビティ17の型面一杯に膨脹させる。

この結果、ネック部14cを除く他の部分が、外層8aと内層18bとからなる2層の中空成形品18が生ずる(第7図)。

なおパリソンの射出成形と吹込成形とを連続的に行う必要がない場合には、射出コア7のエア通路9は不要とし、成形した2層パリソン14を離型

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したのち、射出コア7をコア3に交換して2層パリソン14の成形を行う。

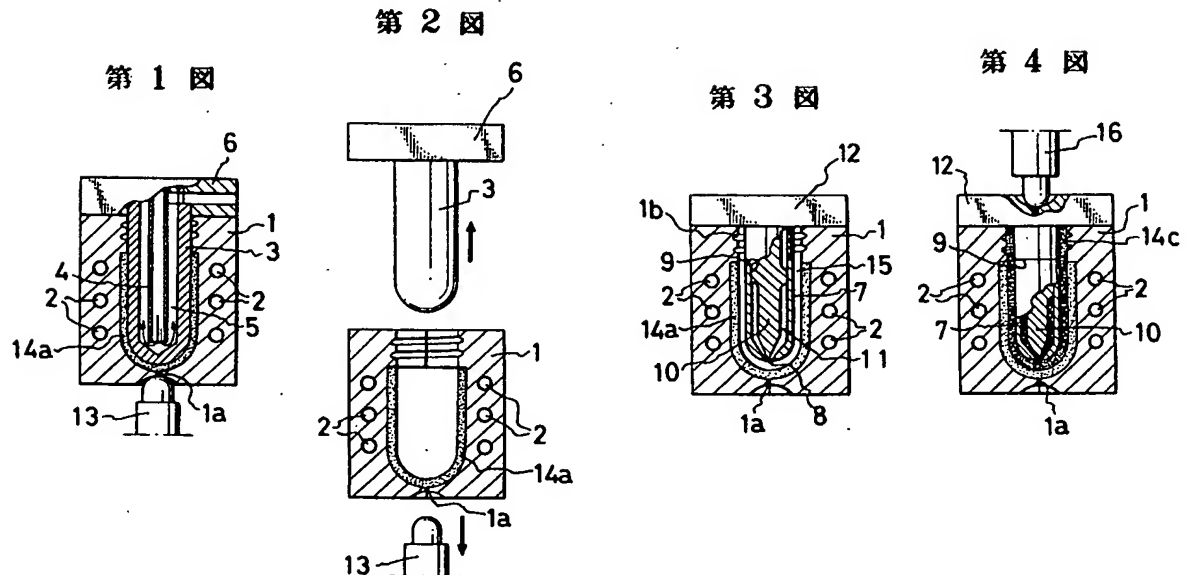
この発明は、上述のように、冷却手段を内蔵したコア3を用いて、外層パリソン14aの射出成形を先行し、上記コア3を射出コア7と交換して、外層パリソンに内層パリソン14bを射出成形したことから、内層パリソンの肉厚を薄く成形することができる。またコアの冷却手段をもつて外層パリソンの内側にスキム層を形成すると共に、底部を固化できるようにしたことから、内層パリソンの成形に際して、外層パリソンが溶解することがなく、内外層が明確に区画された2層パリソンを一連の工程で成形することができる。さらにまた射出成形用のキャビティは1個で済み、コアによる外層パリソンの温度調整も自由にできるため、材料樹脂の適用範囲が広くなり、多くの熱可塑性合成樹脂を2層パリソンに射出成形することができるなどの特長を有する。

#### 4. 図面の簡単な説明

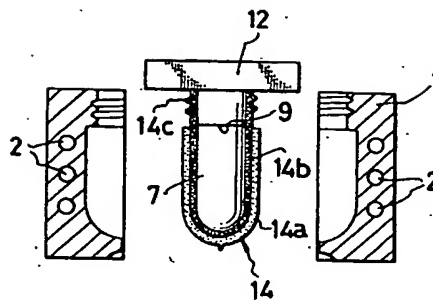
図面はこの発明に係る射出吹込成形における

2層パリソン成形法の1実施例を示すもので、第1図は外層パリソン成形時の断面図、第2図はコア離型時の一部断面図、第3図はコアを交換した際の一部断面図、第4図は内層パリソン成形時の一部断面図、第5図は2層パリソン離型時の一部断面図、第6図は吹込成形時の一部断面図、第7図は2層中空成形品の縦断正面図である。

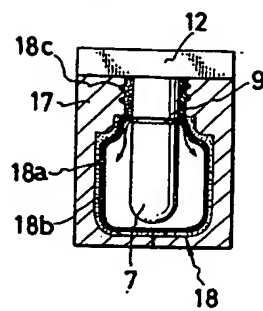
- |             |             |
|-------------|-------------|
| 1……キャビティ    | 3……コア       |
| 4……水管       | 5……冷却水路     |
| 7……射出コア     | 8……射出口      |
| 10……トービード   | 11……溶融材料通路  |
| 14a……外層パリソン | 14b……内層パリソン |
| 14……2層パリソン  | 15……成形空間    |
| 17……吹込キャビティ | 18……2層中空成形品 |



第 5 図



第 6 図



第 7 図

